Annual Reports for 1949-50 of the Chemical Division of the Rubber Research Institute of Malaya

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PREFACE

IT HAS BEEN THE CUSTOM to publish annually the reports of the several Divisions of the R.R.I. together with an introductory survey by the Director.

During the period of recovery after the war, publication of progress reports was delayed. The reports of the Divisions from September 1945 to the end of 1948 were issued as a single publication. Separate publications on specific subjects of research have continued to appear as Communications to the Journal of the R.R.I., but formal Annual Reports have not been published.

Postwar plans for research and development have crystallised and have been formally embodied in the Malayan Rubber Fund Five Years Plan 1949-53. The work of the R.R.I. since 1948 may therefore be reviewed in relation to the general research programme laid down for the five years.

This individual report is one of a number which together will constitute a general report for 1949-51. The whole may thus be regarded as an interim report on the workings of the five years plan. The numbering of sections under the chapter heading INVESTIGATIONS is that adopted in the general research programme.

The Reports for 1949 and 1950 of the Chemical Division are presented. The Report for 1951 was published in October 1952 for expediency.

Director

CHEMICAL DIVISION 1949

RUBBER RESEARCH INSTITUTE OF MALAYA
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STAFF

AT THE BEGINNING of 1949 the graduate staff of the Division consisted of Mr M.W. Philpott (Head of the Division), Mr G.W. Drake, Mr A. Walker, Mr K.C. Sekar and Mr Cheah Sein Liat; together with Drs G.F. Bloomfield and A.I. McMullen, seconded to the Rubber Research Institute from the British Rubber Producers' Research Association; and Mr H.C. Baker, seconded from the laboratories of the London Advisory Committee for Rubber Research.

Mr A.S. Cook, Chemist, took up his duties at the Institute in February 1949 after completing a course of training in the laboratories of the London Advisory Committee for Rubber Research. Mr B.C. Sekhar, Assistant Chemist, was appointed in September.

Just before the end of the year Dr R.G. Newton, British Rubber Producers' Research Association, arrived on secondment to work with other members of the Institute on the technical grading project.

INVESTIGATIONS

INTRODUCTION

ATTENTION WAS GIVEN to the development of the use of paper chromatographic methods for the identification of the non-rubber substances of latex and a start was made by determining the constituent amino acids of the proteins. The method will undoubtedly prove of value in identifying, perhaps estimating, other latex constituents.

Progress has been made in a fundamental study of the nature of the rubber hydrocarbon in fresh latex. The range of molecular weight is a very broad one ranging from 100,000 to several millions. Certain trees, especially ones never tapped, contain a latex which has been termed microgel, in which it is suggested that the hydrocarbon chains are cross linked within the latex particle.

An extractor was designed and built to enable latex to be obtained from the tree under sterile conditions, and in the absence of air. Interesting observations upon the properties of such unusual latex were made.

The Chemical Division, aided by a Malayan Sub-Committee of Latex Producers, collaborated closely in the preparation of a revised British Standards Institution latex standard.

The preservation of latex both temporary and long term has been given attention. After considerable search a combination of chemicals was found which preserved latex in a neutral condition but the process was unfortunately not an economic one. New long term preservatives were tried.

Technological investigations of dry rubber have been concerned with an assessment of the variation between clones and the effect of varying the method of preparation of smoked sheet. A start was made with the incorporation of lignin into rubber and latex.

In September an International Meeting agreed that a survey of Malayan rubber should be made to determine how the French technical classification scheme fitted Malayan rubber production. Three surveys were commenced, but not completed, packing house rubbers, RSS 1 from thirty large estates and RSS 1 from a number of estates selected at random.

Investigations into preparation practices included an experiment in which variations in the technological properties of smoked sheet of similar magnitude to that obtained in the Malayan survey could be obtained by altering the time of dripping of the sheets.

Chlorinated wrapper sheets were used successfully in a shipping trial to the United States.

Advice was given to a group of smallholders commencing centralised manufacture of sheet and in collaboration with the Dutch the first road surface containing Mealorub was laid in Kuala Lumpur.

I
CHEMICAL & PHYSICAL PROPERTIES OF LATEX & RUBBER

(1) STUDY OF NON-RUBBER CONSTITUENTS OF LATEX AND RUBBER

With the two-fold object of characterising more explicitly the latex proteins, and of introducing chromatographic methods into the study of the substances associated with rubber in latex, a separation was made by Mr G.W. Drake of the constituent amino acids of serum protein using the chromatographic method originally described by CONSDEN, GORDON and MARTIN* and perfected by DENT.† Serum which was obtained by successively freezing and thawing fresh latex was dialysed against a cellophane membrane and the non-dialysable portion was hydrolysed with 6% HCl. After removing excess HCl by distillation under reduced pressure, and insoluble humin by filtration, the solution of mixed amino acids

* *Biochem. J.* 38 (1944) 224
† *Biochem. J.* 43 (1948) 169

was applied to a sheet of Whatman No. 1 filter paper and a chromatogram was developed first with phenol and water 70:30. and then with sym. collidine and lutidine 50:50 saturated with water. A 0.1% solution of ninhydrin in butanol was used for locating the spots on the chromatogram.

The mean results for three clonal latices (Gl 1, PB 86, RRI 501) which gave indistinguishable chromatograms are recorded in TABLE I.

TABLE I: LATEX SERUM PROTEIN
CHROMATOGRAPHIC IDENTIFICATION OF CONSTITUENT AMINO ACIDS

No. of spot	R_F *values found*		R_F *values (Dent)*		*Abundance*	*Identity*
	phenol	*collidine/lutidine*	*phenol*	*collidine/lutidine*		
1	0.20	0.11	0.19-0.16	0.2-0.3	++	*aspartic acid*
2	0.30	0.14	0.31-0.28	0.2-0.3	++	*glutamic acid*
3	0.39	0.15	0.38	0.28	+to++	*serine*
4	0.44	0.12	0.42	0.24	++	*glycine*
5	0.53	0.16	0.56	0.27	+	*believed to be histidine*
6	0.60	0.16	0.60	0.27	++	*alanine*
7	0.79	0.05	0.78	0.12	+	*ornithine*
8	0.91	0.08	0.89	0.17	+	*arginine*
9	0.79	0.12	0.82	0.11	+	*lysine*
10	0.86	0.19	0.88	0.28	*present*	*proline*
11	0.78	0.27	0.78	0.36	++	*valine*
12	0.84	0.38	0.84-0.85	0.44-0.48	++	*leucines and phenyl alanine*
13	0.66	0.44	0.61	0.52	*present*	*tyrosine*

The retardation factors (R_F) for the 13 identified constituents agree reasonably well with those reported in the literature (Dent, *loc. cit.*). Two amino acids (cystine and methionine) reported by TRISTRAM* to be constituents of latex protein were not identified; six others not found by Tristram were identified on the chromatogram. Protein fractions obtained by fractional precipitation of latex serum with ammonium sulphate showed no evidence of difference in amino acid constitution.

I(3) RUBBER HYDROCARBON

A method for the rapid estimation of the intrinsic viscosity (and hence the molecular weight) of rubber hydrocarbon was worked out and used extensively for ascertaining the variability in average molecular weight between trees, and the effect of processing and storage on molecular weight of the rubber hydrocarbon. It was

* *Biochem. J.* 34 (1940) 301

found possible to obtain a solution of rubber within a few minutes of its leaving the tree by shaking a few drops of the outflowing latex with benzene and subsequently dehydrating the solution by azeotropic distillation under reduced pressure.

Although significant day to day variation in average molecular weight was observed for a series of individual trees, there was no general trend towards high or low levels during the period March to December, which included a period of heavy rainfall but not a 'wintering' season. The day to day variations were however of little significance compared with variation between trees. The general level of intrinsic viscosity observed in Malaya was rather higher than that observed in Europe.

Fractionation of fresh rubber revealed a broad distribution of molecular weight, the high fractions again having intrinsic viscosities higher than those observed previously in Europe. At the other end of the range the presence of low-molecular fractions, containing small proportions of oxygen in chemical combination with the rubber, was confirmed.

Diffusion into light petroleum without disturbance of the rubber revealed the presence of a gel component in the rubber in freshly tapped latex. The ready dispersibility of the gel indicated that it was of microgel type rather than macrogel as found in rubbers examined in England or in rubbers isolated from old ammoniated latex.

No general correlation was found between the plasticity of rubber and its intrinsic viscosity. Methods of measurement of the former appeared to be very sensitive to presence of gel whereas gel did not necessarily contribute much to the intrinsic viscosity. It is thus possible to select pairs of trees yielding hard and soft rubbers of similar intrinsic viscosity.

Although no significant changes in the intrinsic viscosity of rubber hydrocarbon were observed during coagulation of latex and sheeting, the intrinsic viscosity decreased slightly during smokehouse drying and further decreases were observed on storage of smoked sheet for six months during which the Mooney viscosity increased, softer rubbers increasing proportionately more than hard rubbers.

Latex in untapped or long rested trees was found to contain rubber which appeared to be cross linked within the confines of the latex particle (microgel). Solutions of such rubbers had very low intrinsic viscosity, but the rubbers were certainly not low molecular, being tough and very hard. Variability in intrinsic viscosity was observed in samples drawn from different depths of the

bark, deep sampling giving higher intrinsic viscosities than shallow sampling.

I(4) CHANGES IN LATEX ON TAPPING

Continuing the study of changes in latex involving phosphorus Mr Cheah Sein Liat showed that the total phosphorus content of fresh latex serum is of the order of 50 mgm/100 gm latex, of which 85 to 90% is present as inorganic phosphate. During the first six hours after tapping this proportion does not change significantly—suggesting that the breakdown of the organic phosphorus complex of latex is not a factor in natural destabilisation—but after six days (with 0.1% HCHO as preservative) practically all the serum phosphorus is found to be present in the form of inorganic phosphate. On adding ammonia to fresh latex about 90% of the phosphorus (presumably all the inorganic phosphate) is precipitated; the residual phosphorus content remaining substantially constant over the next few days.

The inorganic sludge which forms in latex on ammoniation is generally held to be magnesium ammonium phosphate; but if the sludge is separated, washed repeatedly with aqueous alcohol and dried, it is found on analysis to have a magnesium: phosphorus ratio of 1 : 1, but to be almost nitrogen free. It is of interest that when a sequestering agent for alkali earths, such as sodium metaphosphate or pyrophosphate, is added to latex before ammoniation the sludge forms very slowly.

I(6) LATEX ENZYMES

In the Annual Report for 1948 reference was made to the presence in fresh latex, or serum, of a phosphatase which promotes the hydrolysis of glycerophosphate at pH 5 to 7. As it seemed possible that this enzyme might play a part in the breakdown of phosphorylated material in fresh latex a short investigation of the characteristics of the enzyme was undertaken by Mr Cheah Sein Liat.

The activities of enzyme preparations were first compared by determining the amount of inorganic phosphate set free after varying periods of incubation at 37° C in citrate buffered mixtures of latex (or serum) and glycerophosphate. In the later stages of the investigation disodium phenyl phosphate was preferred to sodium glycerophosphate because of its higher rate of hydrolysis and because the progress of hydrolysis could be followed by determining either free phosphate* or phenol.†

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* KUTTNER and COHEN *J. biol. Chem.* 75 (1927) 517

† FOLIN and CIOCALTEU *J. biol. Chem.* 73 (1927) 627

Enzyme preparations of high activity and low phosphorus content were prepared by precipitating with ammonium or magnesium sulphate the proteins of acid latex serum. It was found that after discarding the proteins precipitated with ammonium sulphate at one-third saturation the fraction obtained by two-thirds saturation contained the whole of the active material.

Maximum activity occurred within the pH range 5.7 to 6.4 with citrate and 5.2 to 5.9 with acetate buffers.

Phosphatase active sera were obtained when latex was coagulated with dilute acetic acid but not when coagulated with alcohol. Fresh latex and acid serum both became inactive when stored for two or three days, but the activity could be preserved with formaldehyde (0.1%), sodium benzoate (2.0%), or sucrose (saturation). Ammonia caused an immediate drop in activity which was not restored by the addition of magnesium ions. Enzyme preparations were totally inactivated by drying at room temperature; and partially inhibited by zinc, cadmium, copper, and lead ions, and by cyanide. Iodoacetamide was not an inhibitor thus indicating the absence of reactive – SH groups in the system.

The enzyme promoted hydrolysis of glycerophosphate proceeded at an uniform rate during the first forty minutes of incubation at 37°C (up to 8% hydrolysis) but thereafter the rate fell. An experiment to test whether the products of hydrolysis inactivate the enzyme showed that glycerol (up to 50% v/v of the incubation mixture) has no effect on the reaction, but that phosphate (Na_2HPO_4) has a marked inhibiting effect. This would account for the falling reaction rate on prolonged hydrolysis, and also, since the glycerophosphate substrate used in the experiments contained 8% of its phosphorus in inorganic form, the observation that high glycerophosphate concentration reduces the rate of hydrolysis.

To test whether latex phosphatase has synthetic activity, buffered (pH 6.3) mixtures of glycerol (50% v/v) and inorganic phosphate (Na_2HPO_4, 54 mgm phosphorus per litre of incubation mixture) were incubated at 37°C with fresh latex and with fresh latex inactivated by heat. After forty hours there was a drop in the free inorganic phosphorus equivalent to about 20% of the added phosphate indicating that the phosphatase catalyses the synthetic as well as the hydrolytic reaction.

The phosphatase activities of latex serum and of beef kidney extract were compared using disodium phenyl phosphate (D.P.P.) and latex lipoid material as substrates. Both enzyme preparations were active towards D.P.P. but not towards lipoid material. Serum protein was shown to have no lipase or esterase activity. It would

seem therefore that the latex phosphatase does not necessarily play a direct part in the breakdown of latex lipoid constituents.

I(7) MICROBIOLOGY OF LATEX

To study spontaneous physical and chemical changes in latex effectively it is essential to eliminate the complicating factor of bacterial activity. Dr A.I. MCMULLEN designed an apparatus* for extracting latex from the tree under sterile conditions in the absence of oxygen. Although latex extracted with the apparatus was in fact sterile, it did not remain indefinitely fluid. It seems that an enzyme reaction is responsible for the flocculation mechanism in sterile latex. The absence of oxygen from the receiver had no noticeable effect on the stability of the latex. Carbon dioxide was shown to be evolved even after flocculation and some measurements were made on the rate of production of gas from the latex under air and under nitrogen. No oxygen absorption was detected.

II

CHEMISTRY & TECHNOLOGY OF LATEX

(2) VARIATION IN LATEX PROPERTIES

Characteristics of clonal latex — Frequent requests for advice on which clones among those recommended for planting can be relied upon to produce latex suitable for processing as concentrate led to an examination of clonal samples from a variety of sources. Latices of eleven well known clones were drawn from eleven estates and determinations were made of d.r.c., total solids content, cream stability, and content of ash, nitrogen and phosphorus.

From this survey of limited scope it was impossible to disentangle the secondary effects of age of trees and tapping system; the results were therefore inspected only with a view to discovering major differences between clones or between estates. The main indications were that:

a Nearly all clones gave high t.s. content (> 38%) at some estates and low t.s. content (<30%) at others. There was no evidence from this survey that Tj 1, as is some times alleged, gives latex of consistently low t.s. content.

* *Nature, Lond.* 164 (1949) 715

b Latices from R.R.I. Experiment Station all had much higher t.s. content and d.r.c. than latices of similar clone, age and tapping system obtained elsewhere.

c Stability was high for clones PB 186 and Pil B84, low for Gl 1; high for estates No. 1, No. 3 (R.R.I. Experiment Station) and No. 7, and low for estate No. 10.

As the tests indicated that there might be at least as much variability between estates as between clones further samples were taken from two 'high-stability estates' and one 'low-stability estate'. The results confirmed that there are consistent differences between estates with respect to the stability of the latex produced; that clone Gl 1 yields an exceptionally unstable latex wherever it is planted; and that the other clones examined do not differ very much in the stability of their latex (though PB 186 and Pil B84 may perhaps be more stable than average).

The data provided no clear indication of a general relationship between latex stability and the content of ash, nitrogen or phosphorus.

Latex of clone Gl 1 — It is now well established that the latex of clone Glenshiel 1 shows a characteristically low stability whatever the age of the trees and wherever they may be planted. The causes of the instability are not fully understood although evidence is accumulating which suggests that the high ratio of magnesium (a destabilising ion) to phosphate usually found in Gl 1 latex may be a contributory factor.

In our report for 1948* it was noted that the mechanical stability of the latex, as assessed by standard tests, could be effectively corrected by the addition of very small amounts of an ammonium soap, and it was further shown that soaps of the C_{10} (capric) and C_{12} (lauric) normal fatty acids are more effective in this respect than soaps of shorter or longer chain length. These observations have now been abundantly confirmed and latex concentrates have been prepared from Gl 1 latex which, from the point of view of specification properties, are completely normal. The mixed fatty acids of coconut oil, which consist predominantly of lauric acid, provide a convenient source of the required stabiliser.

II(3) LATEX TESTING METHODS

Standard methods of testing commercial latex were reviewed critically from time to time and new methods were investigated. A committee of Malayan latex technologists, convened by the Head

* *Rep. Rubb. Res. Inst. Malaya* (1945-8) 217

of the Chemical Division, continued to advise Sub-Committee RUC/10/7 of the British Standards Institution on the revision of B.S. 902 (Methods of Testing Latex).

Total solids content and dry rubber content — The proposed new standard procedures for determining total solids content and dry rubber content were compared with the existing A.S.T.M., B.S.I. and R.R.I. methods. When these methods were applied to the types of latex for which they were suitable there was no evidence that they gave different results. The main criticism of the proposed new B.S.I. method for determining d.r.c. was that it did not work well with unammoniated or freshly ammoniated latex, whereas the old B.S.I. and R.R.I. methods were applicable to both mature and immature latices. It was accordingly recommended that the new Standard should include an alternative method for use with freshly ammoniated latex.

Alkalinity — For the titration of ammonia in preserved latex the indicator recommended by the B.S.I. is bromthymol blue and by the A.S.T.M. methyl red. Theoretically the latter indicator should give higher estimates of ammonia content than bromthymol blue and the difference between the two estimates should be dependent on the buffer status of the particular latex under test. To determine the order of difference likely to be encountered in practice a representative series of ammonia preserved latices were titrated with both indicators. From the results in TABLE II we see that estimates of ammonia content obtained by titrating latex to the methyl red end point are 0.03 to 0.04% higher than estimates obtained by titrating with bromthymol blue.

TABLE II: TITRATION OF AMMONIA IN LATEX WITH DIFFERENT INDICATORS

All latices containing 0.4 *to* 1.0% *by wt ammonia*

Type	*No.*	*Mean % by wt NH_3 by which estimates with methyl red exceed estimates by bromthymol blue*
unconcentrated	88	0.027 ± 0.011
concentrated	74	0.040 ± 0.013
all	162	0.033 ± 0.014

pH — By a series of laboratory checks it was shown that estimates of latex pH by reference to the glass electrode working in

standard buffer solutions are liable to error because of the inherent instability of most alkaline buffers at 30°C. For a time it was thought the only satisfactory remedy was to set up a normal hydrogen electrode as a standard to which working electrodes could be referred, but it was later found that by taking proper precautions a buffer could be preserved without change of pH for reasonably long periods. The practice finally adopted was to make up freshly each week a glycine buffer solution of pH 11.00 taking care to avoid contact with CO_2 during preparation and storage.

KOH No. — Having established a procedure for determining the pH of ammonia preserved latex KOH titrations were carried out over a period of several weeks on 144 latices and the pH values at inflexion point were recorded. The mean pH at inflexion was 11.225 with a standard deviation of 0.097; range 11.00 to 11.48. In the neighbourhood of the point of inflexion the buffer capacity d(KOH)/d(pH) average 0.15 gms KOH per 100 gm total solids. For the 144 latices examined the differences between KOH No. at inflexion and KOH No. by titration to pH 11.225 ranged from + 0.047 to – 0.061. It is concluded that titration to a fixed end point cannot be substituted for titration to an inflexion point if estimates of KOH No. are required to be within about ± 0.05 of the A.S.T.M. (inflexion) value.

Using the inflexion method, laboratory results were found to be reproducible with a standard error of ± 0.01 gm KOH per 100 gm total solids.

In order to ascertain the rate at which the KOH No. of commercial latex changes with time, portions of a single bulk of latex were preserved in various ways, centrifuged to 60 – 61% d.r.c. and tested at intervals up to five months. The preservative and concentrating treatments were as follows:

A 0.3% NH_3 to field latex; centrifuge; make up to 0.7% NH_3.

B 0.2% formaldehyde; 0.3% NH_3 after one hour; centrifuge; make up to 0.7% NH_3.

C 0.3% NH_3 + 0.15% SP (Sodium pentachlorphenate); centrifuge; make up to 0.7% NH_3.

D Add KOH to concentrate *A* equivalent to its initial KOH No.

The latices were stored in glass bottles in the dark and tested at frequent intervals. The abstracted results given in TABLE III show that each latex increased in KOH No. during the period of the trial in such a way that KOH No. was linear with respect to log time. The KOH No. of latex *A*, for example, could be represented

with reasonable accuracy by

$$\text{KOH No.} = 0.31 + 0.13 \log t$$

where t is the age of the latex in days (from 1 to 148 days).

It is interesting to note that the inclusion of a bactericide (sodium pentachlorphenate) did not affect the rate of increase in KOH No. This suggests that the increase in KOH No. on storage is a result of normal hydrolytic processes and not of bacterial action. The results might have been different if the latices had been subjected to bacterial invasion during the period of storage. The linear relationship between KOH No. and log time may provide a useful means of predicting changes in specification on storage.

TABLE III: CHANGES IN KOH NO. OF CENTRIFUGE CONCENTRATES ON STORAGE

Preservative	*0*	*6*	*28*	*148*
		days		
A *ammonia*, 0.7%	0.29	0.41	0.49	0.56
B *formaldehyde*, 0.2% *ammonia*, 0.7%	0.28	0.40	0.46	0.52
C *SP*, 0.15% *ammonia*, 0.7 %	0.27	0.40	0.46	0.55
D *latex (A) with added KOH*	0.07	0.18	0.23	0.25

Copper — For some it has been suspected that estimates of copper content obtained by following the B.S.I. procedure (dry ashing below 500° C followed by estimation of the coloured diethyldithiocarbamate complex in aqueous solution) are too low. By re-examining each step in the procedure it was shown that the wet digestion method of the A.S.T.M. gives higher and more consistent estimates of copper than dry ashing, though the digestion is slow and reagent blanks are frequently of the same order of magnitude as the amounts of copper found in the rubber samples. Perchloric acid oxidation, though rapid in execution, gives low recoveries of copper. The method finally used was to ash the rubber at 500°C in porcelain or silica after moistening it with concentrated sulphuric acid. The ash was extracted with a mixture of nitric and hydrochloric acids. Interference by iron was prevented by adding citric acid prior to forming the copper diethyldithiocarbamate complex in slightly ammoniacal solution. The colour was extracted with amyl alcohol and examined in a photoelectric absorptiometer.

It is worth recording that silica was preferred to platinum because the latter inflated the results. For the extraction of the ash a mixture of acids was appreciably more efficient than hydrochloric acid alone (HIGH*). The aqueous solution containing the copper complex was made alkaline before extraction with an organic solvent because it was found that under the acid conditions sometimes employed for the extraction, citric acid does not prevent interference by iron. Although carbon tetrachloride and chloroform are the solvents most commonly recommended in the literature for extracting the copper complex, amyl alcohol was preferred to both because it extracts the colour more rapidly than carbon tetrachloride, is less volatile, and unlike carbon tetrachloride need not be dried before making the colour comparison.

Volatile acids — A standard method of assessing spoilage in fish and eggs is to determine the volatile acids obtained by steam distilling a known amount of material. An investigation was started to see whether the method could be usefully applied to the assessment of putrefaction in latex. The procedure adopted in the initial exploratory trials was as follows: A weighed sample of latex (50 gm) is coagulated with sulphuric acid and phosphotungstic acid (to precipitate serum proteins) and an aliquot of the serum is steam distilled at constant volume. Successive 100 ml volumes of distillate up to a total of 500 ml are titrated with standard NaOH.

The sensitivity of the test is indicated by the observation that the V.A. value of an inadequately preserved latex (NH_3, 0.2%) increased by a factor of 30 in the course of one week's storage (KOH No. and conductivity by factors of 3 & 2 respectively), whereas the same latex well preserved (NH_3, 0.7%) showed very little change in these properties.

The extremely high V.A. values obtained with degraded latices suggested that the test might provide a useful measure of putrefactive change, and plans were made to improve and, if possible, simplify the test procedure.

Mechanical stability — Experience of this test tends to emphasise the view that estimates of technical stability obtained by high speed stirring must be interpreted with care. The influence of the age of the latex is well known, but insufficient attention seems to have been given to the variations that can be induced by merely altering the concentration of ammonia in the latex, or by diluting the sample in such a way as to vary the concentration of serum

* *Analyst* 72 (1947) 60

constituents. The effect of these factors is illustrated by the results in TABLES IV and V.

TABLE IV: CENTRIFUGE CONCENTRATE OF 62% D.R.C. WITH VARYING AMMONIA CONTENTS; TESTED 2 DAYS AFTER PREPARATION

Diluted with water to 50% d.r.c. for the test

NH_3 content of original concentrate % by wt	*Mechanical stability min*
0.30	2.7
0.60	4.5
0.90	8.0

The effect of concentration of serum was determined by reducing the d.r.c. of 62% centrifuge concentrate progressively with (*a*) distilled water and (*b*) its own skim (d.r.c. 8.0%), maintaining the ammonia contents of all mixtures at 0.6%. Stabilities were determined on the mixtures without further dilution to a standard d.r.c.

TABLE V: EFFECT ON STABILITY OF PROGRESSIVELY DILUTED CENTRIFUGE CONCENTRATES WITH (*a*) DISTILLED WATER (*b*) SKIM

Ammonia concentration 0.6% on the latex

d.r.c. of mixture %	*Mechanical stability, min*	
	Diluted from 62% d.r.c with water	*Diluted from 62% d.r.c. with skim*
62.0	1.6	1.6
60.0	2.6	2.2
55.0	3.0	2.6
50.0	4.3	3.2
45.0	6.9	4.4
40.0	12.4	8.2

These results not only give a picture of the influence of d.r.c. on the estimate of stability but indicate that the net effect of residual serum constituents is to depress the stability. Where high stability concentrate is required it would therefore seem desirable to centrifuge to a higher d.r.c. than the specification requires and subsequently reduce to specification by dilution with water.

II(4) LATEX PRESERVATIVES

Zinc compounds – In discussing last year the observation that zinc dimethyldithiocarbamate is a preservative for latex (*Rep. R.R.I.*) it was noted that the preservative action was not wholly due to the

anion. Other zinc compounds (oxide, borate, stearate) also showed preservative action when used in conjunction with low concentrations of ammonia. Not only zinc but also cadmium, lead, copper, cobalt, thallium, arsenic, bismuth, mercury, and nickel compounds had the same property. The mechanism of the action is not understood. nor is it immediately clear how the observation may be usefully applied to the preservation of latex in view of the destabilising action of multivalent cations. One possible solution is to treat latex with, say, 0.2% ammonia together with the zinc (or other metal) compound, and then centrifuge after 12 to 24 hours to eliminate excess zinc soaps *etc.* Using this method, latices were kept in fresh, stable condition with 0.2% ammonia for more than six months. Zinc salts in the presence of very low concentrations (less than 0.1%) of ammonia or ethylamine were shown to be effective preservatives for keeping latex in liquid condition for a few days or weeks prior to conversion into sheet or crepe.

Temporary preservatives — The study of short term preservatives (*a*) to prevent pre-coagulation in the field and (*b*) to preserve latex for 1 to 3 days prior to coagulation as sheet was continued. In both applications formaldehyde (0.50 to 0.08% HCHO) is often effective, though difficulties are experienced on wet days and with latex from certain clones. Tests showed that latex preserved with formaldehyde and kept for 3 and 7 days prior to coagulation yielded smoked sheets which were defective in no major respect (appearance, tension strength, modulus, scorching properties) from normally prepared sheet made from the same latex. The trials effectively demonstrated the practicability of storing latex for several days, if necessary before processing as sheet. When formaldehyde alone failed to prevent pre-coagulation in the field, notably in wet weather, promising results were obtained when it was used in conjunction with mild alkalis such as sodium silicate. Recommendations on the use of these anti-coagulant combinations will be issued when the results have been checked and confirmed.

Neutral preservatives — From a mass of empirical data relating to the preservation of latex at pH 6-7 the following general conclusions were drawn:

a The complete preservation of fresh latex at neutral pH requires an efficient colloidal stabiliser together with a bactericide.

b The minimum concentration of each reagent that is required for complete preservation is 0.5 to 1.0% on the latex, so that the total concentration of added materials is 1.0 to 1.5%.

c Ionic stabilisers and bactericides are not generally effective in latex because they are inactivated by reaction with proteins and other non-rubber constituents of the latex.

d Among the most suitable stabilisers found were the non-ionic ethylene oxide polymers; sodium azide was an effective bactericide.

e Latices stabilised with ethylene oxide polymers are heat sensitive and the sensitivity can be adjusted over a range of temperature by suitable addition of salts.

f Coagulation of such latices can be achieved by lowering the solubility of the stabiliser by addition of salt and, if necessary, by the application of heat.

Sodium pentachlorphenate — After several attempts had been made to devise a quick method of determining sodium pentachlorphenate in latex the procedure finally adopted was to ash a weighed amount of latex with lime/sodium carbonate fusion mixture, extract with water and determine chloride by Volhard titration. The determination, though not as rapid as might be desired, could be carried out by a laboratory assistant in three hours with an accuracy of $\pm$ 2%.

Using this method of analysis it was found that in normal latex, to which sodium pentachlorphenate has been added there is a fairly even distribution of preservative between the aqueous phase and the latex particles. Consequently if latex containing, say, 0.2% on the latex of sodium pentachlorphenate is concentrated by creaming, the cream will also contain about 0.2% of preservative. In centrifuging however the concentration of pentachlorphenate in the concentrate was found to be only about 80% of that of the input latex. The greater loss of preservative in centrifuging compared with creaming was attributed to the relatively large surface of the particles which pass into centrifuge skim.

II(5) TECHNOLOGICAL PROBLEMS

Latex creaming — With some latices it is impossible to obtain concentrates of d.r.c. 60% (and a *fortiori* of 62%) by straight creaming. This is particularly true of latices from young plantings or from estates where the average level of d.r.c. is low. Experiments relating to this problem were set up in order to provide a basis for advice to an estate which was having difficulty in producing cream of more than 55% d.r.c. Of the various creaming procedures compared the best and most economical treatment was to cream with the normal concentration of ammonium alginate for four

days, run off the underlayer and stir in a further amount of creaming agent equivalent to a concentration on the water phase of 30% of the original dose. To confirm the efficacy of this procedure a series of low d.r.c. clonal latices were creamed in this way, with the results shown in TABLE VI.

TABLE VI: CREAMING LOW D.R.C. LATEX

Latex (0.6% NH_3) creamed with best concentration (0.1%) of ammonium alginate for 4 days, then for further 10 days after adding 0.03% ammonium alginate

Latex	*drc* %	*4 days creaming*		*4 + 10 days as above*	
		drc %	*t.s.* %	*drc* %	*t.s.* %
Tj 1	34.2	56.04	57.85	63.94	65.60
BD 5	29.3	52.08	53.92	62.64	64.04
PB 86	33.6	53.28	55.22	62.23	63.76
Pil B84	27.4	47.69	49.53	60.00	61.65
Pil D65	27.1	49.95	51.60	60.38	62.05

From these and other results obtained independently it is concluded that the stirring in of a supplementary dose of creaming agent during the creaming period is an effective way of raising the final d.r.c. of the concentrate. The process is probably covered by B.P. 442,964.

Utilisation of skim latex — The possibility of extracting free ammonia from the effluent of latex concentration plants, both as a measure of economy and to facilitate the recovering of rubber from centrifuge skim, was discussed with a firm of chemical plant manufacturers.

Small scale trials were made both in Malaya and in U.K., but the foaming properties of the skim proved to be an insuperable obstacle to its treatment in a distillation plant, and the project was shelved.

Centrifuge skim was successfully converted into a vulcanised crumb of the 'Mealorub' type by heating for 2½ hours at 80°C. with a dispersion of vulcanising agents. The flocculate obtained on acidifying was dewatered by filtration, broken up mechanically into a fine crumb and dried at 50°C. When similar proportions of vulcanising chemicals to dry rubber were employed vulcanisation proceeded more rapidly with skim (d.r.c. 8%) than with freshly ammoniated field latex. With skims of very low d.r.c. the proportion of vulcanising chemicals to rubber had to be increased. Because of the high ratio of water to rubber in centrifuge skim the

heat and tankage requirements are high and it is thought that this might render the process uneconomic on a large scale. There seems to be no reason why the product should be less suitable than 'Mealorub' for incorporating in asphaltic road compositions. Samples were sent to the British Rubber Development Board for inspection.

If skim latex of low d.r.c. is converted into RSS the product is very fast curing and its appearance is usually inferior to that of No. 1 sheet. A series of trials was made to see how much skim latex could be mixed with field latex to produce RSS of good appearance and satisfactory technical properties. One of the objects of the investigation was to find a way of producing sheet for special uses with controlled fast curing properties. Fresh field latex (d.r.c. 37.5%) was mixed with varying proportions of week old centrifuge skim (d.r.c. 4.5%, total solids 8.5%, NH_3 0.52%) to give sheets containing up to 16% of skim rubber. The latices were coagulated in pans with formic acid to give sheets approximately 300 gm in weight. In some of the trials the stoichiometrical amount of formaldehyde was added before coagulation to neutralise the free ammonia. Sheets were also made from fresh latex alone: without ammonia; with 0.5% ammonia; and with 0.5% ammonia neutralised with formaldehyde.

The smoked sheets obtained were analysed for ash and nitrogen (to provide a measure of non-rubber content) and were tested in the A.C.S. mixing.

In general it was found that neutralisation with formaldehyde reduced the amount of acid required for coagulation and improved the quality of the product judged by appearance.

The full results of the vulcanisation tests are not recorded, but TABLE VII is illustrative. Extremely high modulus rubbers were obtained by the addition of skim to field latex, particularly when the ammonia was neutralised with formaldehyde (formation of hexamethylene tetramine). Moderate additions of skim rubber (4 to 8%) slightly increased the resilience of the vulcanisates (due probably to the accelerating effect) but large additions (16%) tended to impair resilience through the introduction of appreciable percentages of protein *etc.*

The results indicate that the preparation of RSS from skim admixed with field latex is not a satisfactory general method of working off skim of low d.r.c. Circumstances in which the method might be successfully employed however are, (*a*) when the quantity of skim relative to fresh latex is small, (*b*) when it is commercially practicable to run the centrifuges to deliver high d.r.c. skim (say

TABLE VII: LATEX SKIM MIXTURES COAGULATED AT 20% D.R.C.

Properties of A.C.S. vulcanisates, 60 min 127° cure

Skim rubber in sample	*Free ammonia*					*Ammonia neutralised with formaldehyde*				
	M_7	*T.S.*	*R*	*Ash%*	*N%*	M_7	*T.S.*	*R*	*Ash%*	*N%*
Nil (no NH_3)	55	131	84.9	0.25	0.40	–	–	–	–	–
Nil (0.5% NH_3)	65	153	87.6	0.24	0.39	142	209	92.4	0.47	0.44
4%	93	172	91.0	0.31	0.53	127	204	90.8	–	0.53
8%	124	202	90.4	0.39	0.64	169	214	92.5	0.45	0.64
16%	154	216	89.1	0.55	0.85	212	221	91.5	0.63	0.91

M_7 – *Modulus at 700% elongation* (kg/cm^2)
T.S. *Tension strength* (kg/cm^2)
R – *Resilience at 70°C* (%)

10%), and (*c*) when there is a special demand for high modulus rubber. In any combination of these circumstances the method might well have practical value.

III

CHEMISTRY & TECHNOLOGY OF DRY RUBBER

(1) MOLECULAR FACTORS IN RELATION TO RUBBER PROPERTIES

Low molecular components were removed from rubber by diffusion into a mixed solvent and the remaining rubber was evaluated technically.

No evidence was found to indicate that removal of the low molecular components effects any significant improvement in the cured rubber.

III(4) TECHNOLOGICAL TESTING METHODS

In order to provide a basis for judging the significance of technological test results Mr Baker investigated the errors inherent in the testing procedures currently used in the laboratory.

The errors associated with the determination of modulus in the standard A.C.S. mix were thoroughly investigated and their magnitude was shown to be satisfactorily small. The variability surveys described in Section III (7) could therefore be carried out confidently without replicating mixings, thus greatly accelerating the rate of testing. Replicated tests were however made on subsamples in order to provide a continuous check on testing errors.

For the evaluation of single tree samples in carbon black compounds a micro-procedure using 30 gm of rubber was developed. The combined errors associated with this procedure were found to be such that observed differences between samples are not significant at the 5% level unless they exceed:

For tension strength, 28 kg/cm^2 (for means of 3 test results)
For modulus at 300%, 7 kg/cm^2 („ „ „ „ „ „)
For resilience, 3.5% („ „ „ 4 „ „)

III(5) VARIATION IN TECHNOLOGICAL PROPERTIES

Because clones Tj 1 and PB 186 are extensively planted and their rubbers differ widely in plasticity they provide useful material for comparing the properties of a hard and a soft rubber. Extensive

technological tests were made on rubber obtained from these clones (R.R.I.E.S. Field 5). The test mixings employed were a tread skeleton and three treads compounded respectively with MPC, RF and SRF blacks. In one set of experiments 5 samples of rubber from each clone were tested twice in four types of test mixing, yielding $5 \times 2 \times 4 = 40$ separate pairs of mixed compound for estimating differences due to clones.

The large mass of data is not recorded here as no clonal differences of technical significance were observed.

Technological tests were also made on sheet rubber prepared from six R.R.I. series clones planted at R.R.I.E.S. (sandy soil) and from four of the same group of clones planted at Bukit Rajah Estate (peaty clay soil). Two clones — RRI 501 and 512 at R.R.I.E.S. — showed statistically significant differences for strength and modulus in both A.C.S. and MPC tread mixes, RRI 512 giving stronger, higher modulus vulcanisates than RRI 501. There was a tendency for Bukit Rajah latex, whether processed at Bukit Rajah or R.R.I.E.S. to give higher modulus rubber than R.R.I.E.S. latex from the same clones. Clone RRI 506 at Bukit Rajah gave exceptionally high modulus rubber ('blue' class in the French classification) and it is thought that this may well have been a soil effect since there is evidence from a survey carried out during the Japanese Occupation (1944) that trees on coastal soils give higher modulus rubbers than trees on inland soils.

In another experiment clonal rubbers from R.R.I. series clones and from commercial (obsolete) clones at R.R.I.E.S. (Field 15) showed considerable variability in Mooney viscosity (range 50 to 119) but little variability in modulus.

The detailed discussion of all the data obtained in these investigations would be tedious and it is sufficient to record that real clonal differences in plasticity and vulcanising properties (confounded with soil, age and season effects) have been observed, but no clear evidence has been obtained of intrinsic superiority or inferiority likely to be of technical importance compared with variations that can be introduced during preparation or manufacture. The results do not encourage the hope of finding important clonal differences for properties such as resilience or abrasion resistance.

III(6) SPECIAL RUBBERS

Purified rubber — Mr H.C. Baker obtained experimental evidence which appeared to support the assertion (MARTIN, *Proc. Rubb.*

Tech. Conf. 1948, 319) that highly purified rubber, when compounded with carbon black, yields exceptionally resilient vulcanisates. The purified rubber used in the experiment was prepared by creaming latex in the presence of soap and successively recreaming it until the concentration of serum substances was calculated to be less than 1% of the original concentration; the latex was then coagulated, creped and dried at 60°C. To a portion of the purified latex was added 0.2% on the rubber of pyrogallol to protect the rubber during drying. Technological tests in loaded and unloaded mixings were made on the purified crepes, and on normal RSS obtained from the same original latex. The whole experiment was carried out with two field latices, Tj 1 and PB 186, both from R.R.I.E.S Field 5.

No important technological differences due to purification were observed except for the property of resilience in a carbon black (RF black) tyre tread compound. It appears from TABLE VIII that purification produces a real increase in resilience, with no appreciable change in modulus or hardness.

TABLE VIII: EFFECT OF PURIFICATION OF RAW RUBBER ON PROPERTIES OF RF TREAD VULCANISATES AT OPTIMUM CURE

Clonal source of latex	*Rubber*	*N%*	*RF tread*		
			M_3	*R*	*H*
Tj 1	*RSS*	0.29	125	63.7	71.3
	Purified crepe	0.05	121	68.4	70.3
	Purified crepe + pyrogallol	0.06	117	69.8	70.3
PB 186	*RSS*	0.30	124	64.3	69.3
	Purified crepe	0.06	117	68.9	69.8
	Purified crepe + pyrogallol	0.06	118	69.6	68.0

M_3 = *Modulus at 300% elongation, kg/cm²*
R = *Resilience at 70°C,%*
H = *Hardness (B.S.I.)*

It could be reasonably contended however that the observed improvement is attributable to the circumstance that the effective concentration of rubber polymer in the tread compound made from purified rubber was higher than in the control, on account of the removal of natural non-rubber diluents during the purification treatment. Towards the end of the year plans were made to examine this possibility, and also to determine the stage in the purification process which is mainly responsible for the observed effects.

Softened rubber – Smoked sheet containing a commercial plasticiser ('Pepton-22D') which exerts its effect only at high temperature was made into miniature bales and heated in a high frequency heating apparatus. The purpose of the experiment, which was carried out in collaboration with a firm of electrical equipment manufacturers, was to show whether the baled rubber could be effectively softened by the user preparatory to mill mastication. The experimental bales were placed between plate electrodes with an applied potential of 9 kv at 11.6 Mc/s giving a voltage gradient in the rubber of approximately 1 kv/cm. Power consumption increased as the temperature of the rubber increased and it is recorded that the bales with plasticiser absorbed about 50% more power than the control bales. The results were disappointing because the heating was neither uniform nor intense enough to produce the softening effect required.

Lignin reinforced rubber — Mr Baker made a short report to the L.A.C. on the technical properties of lignin loaded vulcanisates made by incorporating lignin into rubber (*a*) on the mill and (*b*) at the latex stage. In general, lignin (1 part per 2 parts rubber) retarded vulcanisation and mixings had to be powerfully accelerated, *e.g.* with MBT/DPG, to produce reasonably good physical properties. When solutions of lignin in sodium hydroxide were added to latex (1 part lignin to 2 parts rubber) and treated with excess acid stable pastes were obtained, the properties of which suggested that the rubber particles are completely surrounded by lignin and therefore protected from coalescence. Such pastes might be useful for incorporating rubber into cement. Coagulation of ammoniated latex containing as little as 5% lignin solution gave a filterable paste. It was noted that the incorporation of 2% lignin in rubber delayed the onset of tackiness when rubber was exposed to light.

Arrangements were made with the Department of Scientific and Industrial Research through the London Advisory Committee to provide samples of lignin from different sources so that the investigation might be extended during 1950.

Rubber from heated latex — It has been known for many years* that crepe rubber prepared from latex autoclaved at 145°C is soft, and has low acid value and normal acetone extract, but little is known about the technical properties. Experiments carried out during the year indicated that the main technological characteristics of such rubbers are that they develop high modulus in both MBT and DPG vulcanisates and are extremely scorchy in processing. The chemical changes due to heating which produce

* *J. Rubb. Res. Inst. Malaya* 5 (1933) 302

these technological effects are of considerable interest since it is thought that they might provide a clue to the causes underlying variation in scorching properties.

Hardened rubber — The rubber hardening properties which are exhibited in a marked degree by m- and p- phenylene diamines, benzidine *etc* have been shown to be not confined, as was originally thought, to bi-functional aromatic substances. The toluidines (m- > p- > o-) and aniline, in concentration about 0.5%, all harden natural rubber appreciably.

Two aliphatic substances have now been found which harden rubber; they are urea and ethylenediamine (TABLE IX). As these reagents do not discolour crepe they may have an application in sole crepe manufacture.

TABLE IX: PLASTICITY OF AIR DRIED SHEET CONTAINING ALIPHATIC HARDENING AGENTS

Reagent	D_{10}		*Mooney viscosity*	
	unheated	*24 hr at 60°C*	*unheated*	*24 hr at 60°C*
control, nil	4.72	4.58	85	79
urea, 0.5%	5.03	5.41	106	100
ethylenediamine, 0.5%	4.88	5.54	95	94

The effect of adding up to 2% of urea to air dried sheet is shown in TABLE X: the acceleration of drying by urea referred to in Section IV (1) of this report and in that for 1948 will be noted.

TABLE X: ADDITION OF UREA TO AIR DRIED SHEET

Urea % on rubber	*Drying time at 120°F, hr*	D_{10}	*Mooney viscosity*
Nil	90	4.23	83
0.5	90	4.80	95
1.0	75	4.97	104
2.0	60	5.15	109

Powdered rubber — Rubber powder of the 'Mealorub' type was made on a small scale using variants of the standard procedure. It was shown that the material could be made with equal ease from freshly ammoniated latex, from aged concentrate and from centrifuge skim latex. No difficulty was found in dewatering the crumb in a filter press or in disintegrating the filter cake in a

perforated rod mill of simple construction. As a result of these trials it is believed that the process could be worked efficiently without the aid of the expensive equipment specified in the literature.

A crumb rubber containing 30% of lime was prepared by coagulating fresh latex with freshly slaked lime and passing the coagulum through a creping mill. The product was coarser than Mealorub but might be suitable for application in the same way to asphaltic compositions.

III(7) TECHNICAL GRADING OF RAW RUBBER

At an international meeting held at the Institute in September to consider ways of improving the quality of natural rubber an *ad hoc* committee was set up to consider plans for immediate action and the Head of the Chemical Division and Statistician R.R.I. were deputed to make initial recommendations. An analysis of the statistical problem was made by the Statistician and incorporated in a series of memoranda. Circular letters were sent to 32 estates (over 1,000 acres) and to 6 packers, all in Selangor, Negri Sembilan or Malacca, asking for cooperation in providing samples for estimating the overall variability of Malayan rubber. A questionnaire on preparational methods was also sent to about 200 large estates. From the replies received a selection was made of estates where conditions appeared to favour the production of uniform RSS.

Variability surveys designed to provide basic information on which to establish a technical grading scheme, were started towards the end of the year. Dr R.G. Newton (British Rubber Producers' Research Association) joined the Institute in November on secondment for the purpose of superintending this work. Three surveys had been put in hand by the end of 1949: (*i*) of RSS 1 to 4 drawn from packing houses, (*ii*) of RSS 1 drawn from randomly selected estates (2 sheets from each of 2 bales on 4 days) and (*iii*) of RSS 1 from about 30 large estates which might be expected, by reason of their size and organisation, to be able to participate in a grading scheme on the French model. The surveys were conducted in a manner designed to show clearly whether the French scheme is applicable to Malayan rubber; at the same time alternative methods of test and classification were examined.

At the end of the year about two-thirds of the samples obtained from survey (*i*) had been tested. The results obtained indicated that the French limits for Mooney viscosity classes had been well chosen, about three-quarters of the samples falling into the middle grade and the remainder equally into the hard and soft grades;

but that a preponderence of samples fell into the French low modulus ('red') class and scarcely any into the high-modulus ('blue') class.

III(8) VARIABILITY OF COMMERCIAL RUBBER

Smallholders' sheets of contrasting A.C.S. modulus were comprehensively compared in a MPC tread formula. The results showed that the reinforced vulcanisates were remarkably similar as regards modulus, strength, resilience, hardness, swelling and abrasion loss. Rates of combination with sulphur (widely different in the A.C.S. mix) were the same in the presence of MPC black. The results confirm the previously noted levelling effect of carbon black and help to explain the apparent indifference of manufacturers to the type of natural rubber used in tyre treads.

IV

PREPARATION PRACTICE

(1) PREPARATION OF SHEET AND CREPE

Effect of drying conditions on modulus — HASTINGS and RHODES discussing the results of a variability survey carried out in 1939,* stated 'that the variation in present day methods of preparing sheet is not responsible for as much of the variability as is usually attributed to it'. This conclusion is contrary to evidence obtained in Ceylon (1940-5), and is not supported by the evidence of some of Hastings' and Rhodes' own experiments. For example, TABLE VI in their Communication suggests that variation in rate of cure (in a rubber-sulphur mix) or modulus (in A.C.S. 1 mix) between samples from the same coagulum dried at different estates may be as great as variation in commercial estate sheet. There is indeed a good deal of evidence from various sources which supports the view that a large part of the total modulus or rate of cure variation in commercial RSS 1 is due to variation in conditions of drying. Experiments in Ceylon further showed that variability due to dripping and drying conditions can be minimised by coagulating latex in the presence of formalin. To check this observation an experiment was made in which bulked latex was (*a*) coagulated in the normal way, (*b*) mixed with formaldehyde (0.1% on the

* Communication 243 *J. Rubb. Res. Inst. Malaya* 9 (1939) 200

† Ceylon Rubber Research Scheme Annual Reports 1940-5; *Rev. gen. Caoutch.* 20 (1943) 23

rubber) and coagulated; (*c*) mixed with formaldehyde, kept over night, and coagulated. Portions of the machined coagula were hung to drain at 40°C for varying periods, and then transferred to drying chambers held at temperatures ranging from 40°C to 80°C Finally the air dried sheets were tested (micro-scale) for modulus (M_7) in the A.C.S. test mixing after 60 minutes vulcanisation at 127°C. With 3 latex treatments, 6 dripping periods, and 5 drying temperatures the total number of treatments was 90; the whole experiment was performed twice giving 180 samples for testing. In TABLE XI each recorded modulus is the mean of the two values obtained in the two separate trials.

Two points of immediate interest emerge from TABLE XI namely:

(*a*) The variation in modulus introduced by the different drying treatments used in the experiment is of the same order of magnitude (S = 15.6 kg/cm²) as the variation of Malayan estate sheet found by Hastings and Rhodes (S = 12.3 kg/cm²).

TABLE XI: EFFECT OF PERIOD OF DRIPPING AND TEMPERATURE OF DRYING IN PREPARATION OF AIR DRIED SHEET

Latex treatment	*Dripping time at 40°C. hr*	*Modulus, M_7 of 60 min cure (ACS), kg/cm²*							
		Drying temperature					*Mean*	*Stnd dev.*	*C of V %*
		40°	*50°*	*60°*	*70°*	*80°*			
(*a*) *control*	0	110	93	67	60	65	87.1	15.6	18.0
	3	107	83	67	67	63			
	6	106	93	78	77	70			
	12	106	88	78	78	82			
	24	107	100	97	87	88			
	48	107	108	96	93	91			
(*b*) *0.1%HCHO*	0	57	57	50	52	50	49.9	2.78	5.6
	3	52	52	47	50	47			
	6	53	52	49	46	48			
	12	48	52	47	48	49			
	24	50	49	49	48	46			
	48	51	53	49	46	49			
(*c*) *0.1%HCHO coagulated following day*	0	75	59	66	60	57	67.2	6.26	9.3
	3	81	66	63	65	59			
	6	70	68	62	61	61			
	12	67	68	64	62	68			
	24	78	65	68	66	66			
	48	79	73	72	76	72			

(*b*) Variation due to drying conditions is largely suppressed by the addition of formaldehyde to latex before coagulation.

Since the conditions of dripping and drying on estates are not usually well controlled it is worth considering whether the uniformity of estate rubber could not be improved by the judicious use of antiseptic substances with latex.

Sulphuric acid as a coagulant — The literature on this subject was reviewed and it was concluded that the current belief that sulphuric acid is a harmful coagulant is based on evidence which is open to criticism. A thorough re-investigation was undertaken and a short account of the experiments was tabled at the September meeting of rubber technologists in Kuala Lumpur. The report concludes:

> The published evidence that sulphuric acid produces undesirable qualities in plantation rubber is inconclusive because it is based on obsolete methods of evaluation. An experiment was therefore set up in which rubber coagulated under controlled conditions was tested by methods related to modern technological practice. It was confirmed that sulphuric acid coagulated rubber vulcanises slowly in rubber-sulphur mixings but is not defective in other respects.
>
> A supplementary study of smallholders' sheets coagulated with sulphuric acid and with formic acid failed to disclose any gross disparity between the quality of formic and sulphuric acid samples.

The samples prepared for the investigation will be examined again after a period of storage to determine whether a slow deterioration occurs in sulphuric acid coagulated rubber, as has been asserted by the workers at I.N.I.R.O. Until the investigation is complete no change in the Institute's general recommendations on the use of sulphuric acid will be made.

Accelerated drying of sheet rubber — The observation that protein precipitants facilitate the drying of sheet coagulum* was confirmed and an United Kingdom patent was applied for. Zinc and chromium salts were particularly effective in concentration 0.5% calculated on the rubber, reducing the time of drying of normal sheet by about one-third. No progress was made towards elucidating the nature of the effect.

Packing raw rubber — At the suggestion of a large U.S. tyre manufacturer a 25 ton shipment of RSS 2 wrapped in chlorine

* *Rep. Rubb. Res. Inst. Malaya* (1945-8) 221

treated wrapper sheets was sent to America. The wrappers were chlorinated in the Institute's laboratories by passing sheets of RSS 2 through a bath of water in which a low concentration of chlorine was maintained by the controlled addition of chlorine gas. No method of manipulating the sheet was devised which completely avoided the hazards of the operation and it seems doubtful whether the treatment could be safely applied in packing houses on a production scale. The shipment is reported to have reached its destination in good shape with the shipping marks visible and, despite the absence of bale paint or talc, no adhesion between bales.

ADVISORY WORK

THERE WAS LITTLE CHANGE in the volume of advisory work but senior officers paid more visits to estates than in 1948. More enquiries than usual were received about the colour and quality of sole crepe and the prevention of premature coagulation. Rubber roadway publicity stimulated local enquiry about the preparation of rubber powder.

Several visits were made by the Head of Division and Chemical Engineer to areas where schemes are being developed for the centralised manufacture of smallholders' latex. Office records show the following:

Interviews at the Institute	... 279
Visits to Estates *etc*	... 159
Letters & Reports	... 2,025
Samples examined	... 1,073

Because of the heavy demands on the laboratory's testing and analytical services by commercial firms a new scale of fees was instituted.

Pamphlets issued:

C/AL.12(49) — Shed for Drying Scrap & Lump Rubber
C/M.29(49) — The Simplexometer Chart
C/M.30(49) — Note on New Grades of Plantation Rubber
C/M.32(49) — Methods of Preparing Crumb Rubber
C/M.33(49) — Specified Rubbers
C/M.34(49) — The Use of Hydrometers to Estimate the Rubber Content of Latex
C/M.39(49) — Kuala Lumpur Rubber Road Trials
C/M.43(49) — Carbon Black Test Mixings
C/M.46(49) — Terminology in Rubber Grading

OTHER ACTIVITIES

During the latter part of the year time was spent in preparing plans and specifications of a new factory for the R.R.I. Experiment Station which shall be capable of manufacturing the estate crop as sheet, crepe or concentrated latex, and shall also be easily adaptable for the production of special rubbers and for the investigation of new preparational processes.

Senior officers of the Division attended the international meeting held at the Institute in September to discuss the quality and grading of natural rubber. Informal discussions with delegates from sister institutes held before and after the meeting lasted over a period of about a month. The presence of Dr G. Gee (Director of Research, British Rubber Producers' Research Association) and Mr G. Martin (Superintendent of Rubber Investigations, London Advisory Committee for Rubber Research) at these discussions afforded an opportunity to integrate more closely the planned activities of the R.R.I. Chemical Division, the L.A.C. and the B.R.P.R.A.

The Head of the Division acted as secretary and convenor of a committee of Malayan latex technologists set up to consider changes in latex testing specifications and to advise the British Standards Institution.

In July the Head of the Division with Dr G.F. Bloomfield and Dr C.M. Blow (British Rubber Producers' Research Association) visited the laboratories of I.N.I.R.O., Buitenzorg, Java, to discuss matters of common interest.

Rubber asphalt road trials — With the cooperation of the Kuala Lumpur Municipality trial stretches of asphalt road rubberised by addition of Mealorub were laid in September. The trials were directed by officers of I.N.I.R.O. The R.R.I. Chemical Engineer who was present at the trials made a detailed report which was issued as Chemical Division Memorandum C/M.39(49).

Smallholdings centralised manufacture — The Head of Chemical Division visited Kedah in June, August and September to observe progress at the Merbok & Glugor projects for centralising manufacture of smallholders' rubber. It is a reflection of the benefits which the smallholder derives from centralised manufacture that the amounts of latex offered at Glugor far exceed what the scheme was originally planned to handle. At the end of the quarter, 7,000 to 10,000 lb of smallholders' rubber was being manufactured daily as concentrated latex, sole crepe and RSS. The technical and administrative experience which the scheme provides will assist in planning similar schemes in other parts of Malaya.

Bark disinfectant — In collaboration with the Pathological Division it was shown that a cationic type of fungicide which is known to be an activator of vulcanisation had no effect on the properties of latex rubber when used as a bark spray but appreciably increased the rate of cure of tree scrap.

PUBLICATIONS

DURING THE YEAR the following publication was issued:

Planting Manual No. 9 – R.R.I. - Type Smoke-houses

M.W. PHILPOTT
Head of Chemical Division

Kuala Lumpur
6 January 1951

CHEMICAL DIVISION 1950

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STAFF

AT THE BEGINNING of 1950 the graduate staff of the Division consisted of Mr M.W. Philpott (Head of the Division), Mr G.W. Drake, Mr A. Walker, Mr A.S. Cook, Mr K.C. Sekar, Mr Cheah Sein Liat and Mr B.C. Sekhar.

Mr H.M. Edmondson, Rubber Technologist, joined the Division in August, and Dr R.H. Smith, Biochemist, in October 1950.

Seconded staff comprised the following:

Dr G.F. Bloomfield, *The British Rubber Producers' Research Association.*

Dr A.I. McMullen, *The British Rubber Producers' Research Association.*

Dr R.G. Newton, who left Malaya to return to the *B.R.P.R.A.* in September.

Mr H.C. Baker, who returned to the *London Advisory Committee for Rubber Research* (*Ceylon & Malaya*) in March.

Mr W.G. Wren *L.A.C.*, who joined the R.R.I. in January to take over duties relinquished by Mr Baker.

Mr R.I. Wood, *B.R.P.R.A.*, who joined the R.R.I. in February, to assist Dr Newton and later to take over the work relinquished by him.

INVESTIGATIONS

INTRODUCTION

STUDY OF THE NON-RUBBER constituents of latex has included fractionation of the proteins and isolation of the lipoids. The phosphorus, magnesium and potassium contents of clonal latices have been examined and it is clear that a high magnesium content is not the sole criterion of instability.

Fundamental studies of the nature of the rubber hydrocarbon have progressed well. Microgel latex is composed of particles in which the rubber molecules are cross linked. Low molecular weight fractions containing oxygen have been isolated. Remarkably pure hydrocarbon fractions have been prepared.

In collaboration with B.S.I. latex testing methods have been reviewed especially copper determination and dry rubber content.

A new method for testing putrefaction in latex, the volatile acids determination, has been worked out and shown to be a useful test. In the field of latex preservation formaldehyde was shown to be the most effective temporary preservative. Latex has been preserved for one year near the neutral point by a bactericide and a non-ionic stabiliser. A number of new materials were effective long term preservatives when used in conjunction with ammonia. The instability of Glenshiel 1 concentrate is removed by the addition of small amounts of laurate and phosphate.

Differences were found between the technological properties of clonal rubbers but the differences are unlikely to be of commercial importance. Removal of the low molecular weight hydrocarbon fraction did not improve the properties of the remaining rubber while very high molecular weight rubber gave no appreciable improvement in properties. Preparation practices also had little effect.

A major effort was made to establish technical classification of Malayan rubber. The surveys commenced in 1949 were concluded and showed that there was a large variation between estates and between sheets within a bale but bale samples taken along the edge of a bale remained reasonably uniform for each estate. In packing houses and remillers, however, there was a large day to day and between bale variation necessitating a blending system. The majority of Malayan rubber was medium Mooney viscosity (circle) and low modulus (red) when classified according to the original French proposals. Junior staff have been trained to operate a testing station and a first shipment of 65 bales was made to U.S.A. for manufacturer's evaluation. Testing methods have been assessed for error.

Other technological investigations included the production of carbon black masterbatch by coprecipitation of carbon and rubber. Lignin masterbatch gave interesting results.

Among preparation practices investigated have been the effect of clarification and the effect of the use of sulphuric acid as a coagulant upon the properties of the rubber. The bleaching action of mercaptans on the yellow pigment of latex has been patented and steps taken to assure commercial supplies of the bleaching emulsion.

Plans were begun to erect a new factory at the Experiment Station. It was shown that a line ahead creping battery was feasible but the continuous coagulation process originally developed with old ammoniated latex did not work with fresh latex.

I
CHEMICAL & PHYSICAL PROPERTIES OF LATEX & RUBBER

(1) NON-RUBBER CONSTITUENTS OF LATEX AND RUBBER

The application of chromatographic methods to the study of substances associated with rubber in latex, was commenced in 1948. Attention was directed mainly to the study of amino acids contained in serum proteins, and the identity of a number of the acids was established. During the past year, chromatographic studies have shown no evidence of the presence of peptide fragments in fresh acid serum or in dialysate from fresh serum, as might be expected if amino acids were derived from protein degradation processes occurring in the latex. Fractionation methods for protein separation were developed later in the year, however, which permitted the isolation from serum of certain protein fractions giving reactions for proteose; fractions were also isolated giving reactions for albumin, globulin and peptone.

An examination of lipoid material isolated from latex, by the method of Rhodes & Bishop, has shown that the yield and composition vary according to the source and age of the latex and to the preservative employed. Material from sodium pentachlorphenate latex was deficient in nitrogen and phosphorus, the content decreasing as the latex was stored; the total amount of lipoid material obtained from the latex increased during storage. The material had a high acid value, but contained few saponifiable substances, which suggests that breakdown of complex lipoid material occurs readily in sodium pentachlorphenate preserved latex.

The occurrence in latex of glucose was established, and the presence of polyphenol oxidase probably in association with an inhibitor of a proteinic nature was confirmed. Attempts to demonstrate the presence of phenolic substances (Pauly reaction) were unsuccessful.

I(2) VARIATION IN NON-RUBBER CONSTITUENTS OF LATEX

Latices from clones RRI 501 and Pil B84 were collected from two estates and analysed for potassium, phosphorus and magnesium content; no significant difference between clones or estates could be found for phosphorus or potassium but latex from Pil B84, which is relatively stable, had a higher content of magnesium than latex from RRI 501, which is relatively unstable. This observation is of interest in connection with latex of clone Gl 1 which, besides

being very unstable, usually has a high magnesium content. It is clearly an over simplication to ascribe the inherent instability of certain clonal latices to high magnesium alone.

I(3) RUBBER HYDROCARBON

Molecular weight studies on the rubber hydrocarbon have been extended using Zimm-Meyerson osmometers. The work has led to the interesting observation that, in latex from a freshly opened cut, there exists a hydrocarbon fraction which has an abnormally high 'osmotic' molecular weight, and yet shows a low 'viscosity' molecular weight; the rubber is very hard. This is characteristic of a 'micro-gel' structure, and can be explained by the existence of a relatively high degree of cross linking of the hydrocarbon within the latex particles. As tapping proceeds the properties of the hydrocarbon change, until after some four or five tappings they have reached the level normally experienced; there is evidence that with still further tapping, microgel latex is slowly withdrawn from a large area of bark.

A slaughter tapping experiment in which latex was examined separately from two cuts, has shown a marked difference in properties of the rubbers obtained, that from the freshly opened upper cut being hard and remaining so as tapping proceeded, whilst that from the lower cut became progressively softer. The lower cut was fairly effectively isolated from the upper part of the tree, by the expanded V top cut; the results thus suggest that whereas the upper cut can draw upon reserves of microgel latex from the tree, the lower cut cannot.

Viscosity measurements on rubber from normally tapped trees have shown that there is no marked change in the average molecular weight from a given tree throughout the year, not even during the wintering period. The distribution of molecular weight in rubber from a single tree is wide, and values extend from 0.1×10^6 to 3×10^6; much of the hydrocarbon is in the high range. An oxygenated fraction with a molecular weight of about 50,000 was also shown to be present. It was observed that fractionation of the rubber hydrocarbon using a solvent pair precipitation method gave rise to very pure hydrocarbon samples, with a nitrogen content of about 0.01%.

Degradative changes occurring in the hydrocarbon during the estate manufacture of smoked sheet were found to be very small.

In the course of this work, it was observed that acetone extraction gave rise to a marked increase in hardness and recovery of rubber, as measured by the William's plastometer. Replacing

the acetone soluble material caused a return to the original, soft condition.

It has been reported in the literature that, when the large and small particles of latex are separated by centrifuging, the large particles yield a harder rubber than the small particles. Experiments designed to confirm this observation showed the opposite, rubber from small particles being harder and having a higher solution viscosity than rubber from large particles. Abnormally hard rubber was also obtained from purified centrifuge skim.

I(6) ENZYME ACTIVITY

The technique for collecting latex from the tree under sterile conditions has been further developed, so that the latex may be passed directly into respirometers of the Warburg type, which permit observations of gas evolution or absorption to be made. Preliminary work indicates that no absorption of oxygen occurs under completely sterile conditions. Evolution of carbon dioxide takes place as soon as latex leaves the tree, but is probably confined to the yellow fraction, which appears in general to be the origin of changes leading to instability of the latex.

II

CHEMISTRY & TECHNOLOGY OF LATEX

(1) LATEX AS A COLLOIDAL SYSTEM

Preliminary work on the structure of fresh latex coagulum, showed that the tension strength slowly increases on standing, during which time syneresis of the gel occurs; this stage is followed by a rapid change in strength after long periods of standing, during which stage microscopical studies suggest that the particulate nature of the original coagulum is lost. The rate of loss of water from the coagulum is increased by addition to the latex of materials which displace protein from the surface of the particles.

II(3) LATEX TESTING METHODS

Dry rubber content — Experiments have been carried out to determine to what extent the d.r.c. of latex is affected by ammoniation. The mean change in d.r.c. values before, and 20 hours after adding ammonia gas, differed significantly from zero, but could be attributed to the dilution effect of the added ammonia. No changes in total solids content were detected. It was concluded that apart

from dilution effects, the presence of ammonia does not influence the determination.

Trials are in hand to establish a rapid method for determining d.r.c., in which the latex sample is withdrawn by means of a dipper delivering a known volume.

Dry rubber content and specific gravity – A re-examination of the specific gravity/dry rubber content relationship for ammoniated latex concentrates indicated that values computed by FAIRFIELD SMITH* from data obtained in 1934 by RHODES† may be too low, particularly for latices of d.r.c. higher than 58%. From six parent latices, concentrates ranging in d.r.c. from 46% to 66% were prepared by mixing high d.r.c. centrifuge concentrate with its own skim. Specific gravities (d_{29}^{29}) were determined and regression equations were calculated from the data. As the regressions for the six parent latices did not differ from one another significantly they are pooled, to give:

$$d_{29}^{29} = 1.01321 - 0.001126 \ (\% \text{ d.r.c.})$$

For 60% concentrate this equation gives $d_{29}^{29} = 0.9457$ which is appreciably higher than the figure 0.9433 obtained by Rhodes and Fairfield Smith. From records supplied to the R.R.I. by two large latex producers it seems that the best values for centrifuge concentrates now shipped from Malaya may be lower than those obtained in the present investigation and higher than those of Rhodes.

Volatile acids – Further work on the determination of volatile acids, has indicated that the method can be a valuable guide to the degree of putrefaction occurring in latex. Steam distillation is employed for removing the volatile acids from serum (obtained by coagulation with sulphuric and phosphotungstic acids); the acids in the distillate are then estimated by titration. They comprise acetic acid chiefly, together with formic and propionic acids. The acids form in inadequately preserved latex, for instance in latex containing 0.2% ammonia, and occur almost entirely in the aqueous phase; the development can be arrested by increasing the ammonia content to 0.7%, or by adding other anticoagulants, such as sodium pentachlorphenate, sodium bisulphite or formaldehyde. It has been shown that very little volatile acid is formed in latex from which serum substances have been removed by repeated creaming, and evidence had been obtained that the acids are derived from the carbohydrates (*e.g.* quebrachitol and glucose) in the serum rather than from the proteins.

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* *J. Rubb. Res. Inst. Malaya* 9 (1940) 218

† *J. Rubb. Res. Inst. Malaya* 5 (1934) 234

Copper — Methods for determining copper in latex have been compared; in the course of the work it was shown that interference by iron (ferrous or ferric) up to an iron/copper ratio of 20:1, can be completely suppressed by treatment with citric acid.

Conductivity and stability — Attempts to establish a correlation between conductivity and mechanical stability of latex were not successful, as the relationship was found to be a very irregular one.

II(4) LATEX PRESERVATION

Pre-coagulation — Little is known regarding the causes of pre-coagulation in the field. An interesting observation, made in the course of work on this problem, was that the aqueous extract from *Hevea brasiliensis* bark markedly accelerated coagulation. This confirms the suggestion made by PATON* that bark substances may affect latex from wet trees. The activity of the bark extract was not reduced by sterilising, thus suggesting that the effect was not due to enzymic activity.

Temporary preservatives — As a temporary preservative sodium bisulphite was found to be more effective, weight for weight, than sodium sulphite. Formaldehyde in the presence of mild alkalies, such as carbonates, silicates and phosphates gave very effective temporary preservation. Sodium pentachlorphenate was ineffective at concentrations up to 0.2%, both with and without mild alkalies. Evidence has been accumulated which suggests that if the lutoid fraction could be efficiently eliminated from field latex, neutral preservation of latex would not be impracticable.

Neutral preservatives — Work on the preservation of fresh latex at, or near the neutral point, has led to a number of interesting conclusions, which may be summarised as follows.

With incomplete preservation of latex, it appears that the yellow fraction coagulates first, the remainder of the latex often remaining liquid for a long period. Observations have shown that divalent cation sequestering agents, at high concentration, can maintain latex in a fluid condition for long periods of time.

Bactericides and emulsifiers of the ionic type, which have been found efficient in other fields, are often very ineffective in latex, probably due to interaction with serum proteins. Non-ionic stabilisers are considerably more effective, especially if a bactericide, such as sodium azide is also present, samples of latex having

* *Chem. & Ind.* (*Rev.*) 58 (1939) 246

been maintained in a completely liquid condition for more than twelve months, at a pH level of approximately 6.5. The difficulty with this type of stabilising system is, in fact, in producing coagulation of the latex when required, normal methods being ineffective. Apart from this consideration, the cost of the reagents required would at present make the process impracticable for commercial use.

New preservatives — Trials were carried out with a number of reagents as preservatives in the presence of 0.2% ammonia; the following were effective in maintaining latex in a liquid condition at the concentrations given: Santophen I (o-benzyl p-chlorphenol) 0.1%, dichlordihydroxydiphenylmethane 0.1 – 0.3%, a dyestuff based on flavine 0.01 – 0.1%, certain acridine dyes 0.01%. A more detailed examination of latices containing these preservatives is now being made.

II(5) TECHNOLOGICAL PROBLEMS

Sodium pentachlorphenate — Sodium pentachlorphenate is well established as a preservative for latex when used together with ammonia. An objection to its use, however, is that it causes discolouration in latex films. Experiments have shown that this may be suppressed by the addition of 0.1 – 0.2% of sodium bisulphite, or by increasing the alkalinity of the latex by adding a fixed alkali. It was also demonstrated that the pentachlorphenate had no appreciable effect on the light ageing of films of dried latex.

The addition of sodium pentachlorphenate to ammonia preserved latex markedly increases mechanical stability. Examination of allied substances showed that certain compounds enhanced stability, whereas others had the reverse effect, *e.g.* sodium o-benzyl p-chlorphenate. Experiments to determine the distribution of a number of chlorinated phenolic compounds between the rubber and aqueous phases, indicated that certain phenols are strongly adsorbed by latex particles and tend to decrease stability, whereas others are absorbed to a lesser extent, and increase it.

Unstable latices — Although the mechanical stability of latex is enhanced by the addition of ammonium soaps, the zinc oxide stability is scarcely affected; it is considerably improved, however, by the addition of phosphates. A latex that is defective in both mechanical and zinc oxide stability should therefore be capable of rectification by the addition of soap and phosphate. Experiments in which these reagents were added to the unstable latex from clone Gl 1, showed a marked improvement in both types of stability. By interchanging sera from Gl 1 and seedling latices, it

was demonstrated that the cause of instability is associated largely with the aqueous phase. Further work suggested that the effect of adding phosphate was connected with the presence of magnesium ions, and that the ratio between phosphate and magnesium may play an important part in determining the stability of natural latex.

III

CHEMISTRY & TECHNOLOGY OF DRY RUBBER

The major part of the work carried out in the rubber technology laboratories has been concerned with the project to establish technical classification of Malayan rubbers. This has been based on surveys of three types of production, comprising estate and packing house sheets and remilled crepes. Many ancillary investigations have also been made, directed towards solving problems arising in the course of the main investigation.

Apart from work on classification, the problems investigated have been largely directed towards studying the naturally occurring variations in raw rubber, with a view to obtaining an improvement in quality.

III(5) NATURAL VARIATION IN RUBBER

Investigation of rubber from individual clones was continued during the early part of 1950. The object of this work was to determine whether differences in the technological properties of the rubbers were sufficiently marked to warrant the selection of certain clones for planting or for the development of new clonal material. Significant differences have been observed in modulus and resilience of MPC tyre tread vulcanisates prepared with the rubbers, but it is unlikely that the differences were sufficiently marked to be of commercial interest.

Differences occurring between rubbers are thought to be due largely to non-rubber substances; differences in the rubber hydrocarbon, for example in molecular weight, are also likely to occur and recent experiments have been directed towards determining whether these variations are of importance. Rubber from a single tree was prepared (*a*) as smoked sheet, (*b*) as acetone-extracted crepe from latex purified by soap treatment and repeated creaming, and (*c*) as (*b*), with the low molecular weight hydrocarbon fractions extracted by benzene/ethanol under nitrogen. Purification reduced the modulus of an unfilled vulcanisate, but increased

the resilience of a tyre tread stock, thus confirming previous observations. Removal of the low molecular weight fraction had little effect upon modulus or resilience.

When smoked sheet is prepared with latex from newly opened tapping cuts, the rubber hydrocarbon is found to be hard and of very high molecular weight. As tapping proceeds, the hardness and molecular weight of the rubbers decrease and approach normal values. Examination of RF tyre tread vulcanisates prepared from such a series of rubbers showed that high molecular weight made no appreciable difference to properties, although differences in processing behaviour were observed.

Evidence so far, thus indicates that differences due to the presence of low or high molecular weight hydrocarbon in smoked sheet are not of great significance with regard to technical properties.

Although the differences between clonal rubbers may not be great, variability due to this factor and many others, renders supplies of commercial rubber open to considerable criticism, and experimental work has been undertaken in an attempt to examine certain of the underlying causes of variability in greater detail. A study of weather conditions immediately preceding and during tapping is being made; preliminary results suggest that certain observed factors have a significant effect. Collecting latex in clean or dirty cups, appeared to have no definite influence upon the rubber obtained; the addition of a bactericide to the cups, with a view to preventing infection, also had no appreciable effect.

III(6) SPECIAL RUBBERS

Lightly vulcanised crepe — It is claimed that the processing qualities of butadiene-styrene synthetic rubbers are improved if the polymer is lightly cross linked by replacing part of the styrene by divinyl benzene. By analogy, it might be inferred that the processing of natural rubber would be altered, perhaps with advantage, by the introduction of a small degree of cross linking, for example, by very light vulcanisation. This possibility has been tested by co-precipitating fresh and vulcanised latex in different proportions.

The crepes produced were of normal appearance, with improved resistance to light ageing. On milling, the rate of breakdown was unaffected by the addition of 20% of vulcanised rubber; with 40%, a small decrease in the rate of breakdown was observed. The properties of vulcanisates were somewhat changed, the rubber showing increasing modulus values with increasing proportions of vulcanised latex; this may have been due to interaction

between the reagents used for vulcanising the latex in the first instance, and those added on the mill for normal compounding. Trials of processing properties have yet to be carried out.

Centrifuge skim rubber — Examination of smoked sheet prepared from latex skim revealed high modulus for mercaptobenzthiazole vulcanisates and low modulus for diphenyl-guanidine, as compared with ordinary RSS. Similar properties were found to be conferred on normal smoked sheet by the addition of nitrogenous bases and fatty acids.

Carbon black and lignin masterbatches prepared from latex — Sheets containing 50 parts of MPC or RF black have been satisfactorily prepared by co-precipitating carbon black dispersions with latex. The sheets had a clean handle, provided a finely dispersed black slurry was used, such as that obtained by ball milling. Tyre tread vulcanisates prepared from the sheets by milling in vulcanising ingredients showed properties similar to those of dry mixed stocks prepared from the same basic materials.

A certain grade of lignin (Indulin A of Canadian origin) was found to behave as a reinforcing agent for rubber when added to latex as a solution in sodium hydroxide, the mixture then being precipitated with acid in the usual way. Although showing good tension strength and fairly high modulus, the vulcanisates were very hard, and showed a high permanent set after extension. The method of preparation is not a practical one, owing to the large amount of acid coagulant required to neutralise the alkali used in dissolving the lignin, but the results are interesting in so far that they indicate the possibility of obtaining reinforcement with this material.

Rubber powder — Modifications of the method published for the preparation of rubber powder, 'Mealorub', have led to a number of interesting observations. Sulphuric acid may be used as a coagulant in place of formic acid, the resulting crumb showing less deterioration after exposure to sunlight or after heating for long periods at 55°C. Although the original Dutch claim stated that fresh latex should be used, the powder has also been prepared quite satisfactorily from two years' old ammoniated concentrate. Unconcentrated, freshly ammoniated latex was found to show excessive thickening on heating with the vulcanising dispersion. Satisfactory preparations were also obtained using centrifuge skim of less than 12% d.r.c., but it was found necessary to increase the proportion of vulcanising ingredients to rubber. It was found possible to carry out vulcanisation at room temperature by using zinc

dibutyldithiocarbamate as an accelerator; the time required was fifteen days.

III(7) TECHNICAL CLASSIFICATION OF NATURAL RUBBER

Main investigation — At an international meeting held in Kuala Lumpur in September 1949, a Committee was set up to deal with the problems of improving the quality of natural rubber, more particularly with a view to establishing technical classification of Malayan exports. Work on the problem was at once initiated in the R.R.I. laboratories and the findings have been reported at intervals to the Committee; two meetings were held during 1950, one in March and one in August, when reports of the investigations were considered. At the March meeting it was recommended that a Testing Station should be set up at the R.R.I. for purposes of grading Malayan rubber; towards the end of the year, the station was nearing completion and suitable junior staff had already been trained. At the August meeting it was recommended that all organisations in the country connected with rubber producing and marketing, should be invited to give their views on the setting up of an organisation to act as the Malayan authority on technical classification. This recommendation was carried out and the general opinion expressed was that it would be premature to establish a producer's organisation at that time.

The experimental work carried out by the Rubber Research Institute comprised surveys of three main sources of rubber, designed to study the variability of, (*a*) estate sheet (1,264 samples from 71 estates), (*b*) sheet from packing houses (358 samples from 6 houses and 90 samples from 5 houses) and (*c*) rubber from remillers (128 samples from 3 factories). Although the surveys had been put in hand by the end of 1949, sufficient results to give an estimate of the general position were not available until mid-1950; further surveys investigating certain aspects, such as the effect of seasonal changes, smallholder's rubber, and so on, were still in progress at the end of 1950.

Rubbers were at first sampled by taking sheets at random from 'bales' before packing; later this was replaced by cutting portions from the finished bales, which was thought to give better representation. Each sample was then examined for two properties, (*a*) the Mooney viscosity of the raw rubber, which was intended to give a measure of the technical processibility of the material, and (*b*) the modulus developed in the A.C.S. No. 1 compound under standard vulcanising conditions, which was designed to

indicate the vulcanisation behaviour likely to be experienced under manufacturing conditions.

The surveys have indicated that for estate RSS 1 the major source of the variability lay between estates; variation from day to day within an estate was also considerable when estimated from sheet samples, the estimate being reduced when bale sampling was adopted. On any one day, the variation between bales was not significantly greater than that within bales. Variation within bales was less for large than for small estates.

With packing house sheet (RSS 1 to 4), on the other hand, differences between packers were small; day to day variation and, on any day, variation between bales, were considerable.

Remilled rubber (Thin Remilled Nos. 1, 3 & 4, C & D Blanket, Flat Bark and No. 1 Compo) also showed fair uniformity between consignments of the same grade from different remilling factories, but there was significant day to day variation in the product of any one factory. The biscuits (folded lengths of crepe) comprising a bale were found to show highly significant differences one from another, but each biscuit showed remarkable uniformity throughout its length.

Comparison of the level of properties of rubbers from different sources showed that crepes from remillers gave the highest Mooney values (*i.e.* were the hardest rubbers), with the exception of flat bark crepe which was soft; further examination, however, showed that although remilled rubbers were harder, they broke down more easily than smoked sheet when masticated on the mixing mill. For packing house rubbers, RSS 4 was harder than RSS 1. Estate RSS 1 tended to be harder than the same grade from packers. The modulus of RSS 1 from estates was higher than that of RSS 1 from packers. RSS 4 from packers, however, showed a still higher modulus value. Remilled crepes invariably showed a low modulus.

The distribution of Malayan rubbers, according to the three classes of hardness (line, circle, cross) and three classes of modulus (red, yellow, blue) proposed in the original French scheme for 'caoutchoucs specifiés', was ascertained after completion of the main surveys. With regard to hardness, the majority of smoked sheet rubbers will probably fall in the circle group (medium hardness), with smaller quantities occurring both in the line and cross classes. With regard to modulus, the distribution is such that a preponderance of Malayan rubber will fall in the red (low modulus) category. The situation with regard to modulus, however, will

be changed after January 1 1951 when the modulus test method used in the original French specifications is to be modified in accordance with a decision taken by the International Rubber Research Board. This follows a resolution of the International Standards Organisation meeting at Akron, October 1950, in which the modulus of ring test pieces was defined as measured at an elongation based upon the mean circumference of the ring; the test as used in the original French specification was based upon the inner circumference. The effect of the change will be to shift the distribution of Malayan rubber production towards the yellow and blue classes (medium and high modulus).

In the course of the work a number of interesting problems were investigated. On one estate, which was laid out in clonal blocks, a bulking trial was carried out comparing sheets prepared when the latex from each block was coagulated separately with those produced by bulking all the latices before coagulation. In this case bulking brought about a marked improvement in uniformity and indicated that the principle of large scale bulking is a sound one.

A decrease in the bale to bale variation of packing-house rubber was demonstrated by introducing a modification of the method of packing, in which sheets from a number of different incoming lots were deliberately selected for building each bale.

As a practical outcome of these investigations a small shipment of 65 bales of classified rubber was shipped to the U.S.A. towards the end of the year; it is hoped in due course to receive manufacturers' reports on the rubber.

Testing methods — Characterisation of the processing properties of raw rubber is not an easy matter and the use of the Mooney viscometer for this purpose has been criticised on the ground that it does not correlate at all closely with rate of breakdown during mastication. Further work has shown that rubbers of the same initial Mooney viscosity break down to different values under standard conditions of mastication, thus confirming the relative insensitivity of the test as a guide to processing behaviour.

Interlaboratory comparisons made with Mooney instruments showed the need for a standard material to cross check instruments in different laboratories; the tendency of natural rubber to change during transit or storage render it unsuitable. Polyisobutylene, although constant in properties, can be used to check only the lower ranges of the instrument.

For purposes of determining modulus, experiments showed that the method of assessing test piece dimensions using weight

and density was less subject to random error than that employing direct measurement by gauge. Comparison of Schopper modulus determination (using this method of measuring dimensions), with a simple strain tester measuring elongation under a given load (developed by the B.R.P.R.A.), showed that a satisfactory correlation existed between the two quantities for rubbers freshly tested under Malayan conditions. This should enable a relatively cheap and simple method of test to be used for assessing the modulus of rubbers, thus facilitating both the equipping and the procedure in testing stations, set up for the purpose of classification.

It was reported from the B.R.P.R.A. laboratories that strain values of a given vulcanised rubber were dependent upon the viscosity of the unvulcanised stock and that a correction should be applied to allow for this factor when comparing different rubbers. Application of such a correction entails determinations of strain at two levels of viscosity of the compounded stock, thus involving a considerable amount of extra labour, if used for routine testing. Preliminary attempts to develop a means of correcting strain on the basis of a single determination viscosity suggested that the errors involved would offset any advantage that might otherwise be gained.

An examination of the errors associated with mixing, curing and testing operations showed that for strain and modulus values the error was correlated with the level of the property measured. In Mooney viscosity determinations no correlation with level was found for the range 70 to 100 units. Serious errors were demonstrated in the Mooney test when certain rotors were employed; it was shown that even if conforming to dimensional specifications, imperfect finish of the edge grooves was liable to cause important differences in the values obtained.

In carrying out routine testing operations it is important to standardise conditions and at the same time to avoid unnecessary delays. The practice in the R.R.I. laboratories is to carry out the operations of mixing, curing and testing on three consecutive days, which conforms with the schedules laid down by recognised standards institutions. Difficulties of organisation are involved, however, at weekends and public holidays and experiments to determine the effect upon modulus of the time of storage between the different operations have been carried out. It was shown that departure from a standard procedure may lead to significant differences in the values obtained, and there was no evidence that a simple correction to allow for a known change of procedure could be adopted with any degree of certainty.

IV

PREPARATION PRACTICE

(1) EFFECT UPON SMOKED SHEET OF TEMPORARY LATEX PRESERVATIVES

Ammonia and formaldehyde are the two most commonly used short term preservatives; of these, ammonia is more effective in wet weather, but it has a disadvantage in that it increases the variability of vulcanising behaviour in smoked sheet prepared from latex to which it has been added. Formaldehyde, on the other hand, decreases variability. It has been shown that latex preserved with 0.1% formaldehyde (which quantity is usually adequate for overnight preservation) yielded sheet differing in no essential respect from standard RSS, when used for tyre tread or sidewall compounds, although a slightly lower modulus was observed in certain cases with an unfilled mix. The use of ammonia was found to increase the modulus of vulcanisates. Formaldehyde and ammonia together gave good preservation and were without effect on the vulcanising properties of the sheet produced.

Accelerated coagulation — Trials to determine whether coagulum can be sheeted within a short time of preparation, showed that by working with latex at 20% d.r.c. and using the normal dose of formic acid, coagulum is obtained which can be machined two hours later without difficulty. This seems to be a simple solution to the problem of utilising coagulating equipment more than once a day.

Effect of drying conditions on modulus — Continuing experiments carried out during 1949 confirmatory evidence was obtained that variable drying conditions may be an important source of modulus variation in sheet rubber. The addition of formaldehyde to latex was shown to suppress variations of this kind.

Sheet from clarified field latex — Several experiments have been undertaken during the past year to ascertain how latex and dry rubber are affected when fresh latex is subjected to centrifugal clarification, using an Alfa-Laval machine.

Examination of latices, to which ammonia had been added after treatment, showed that clarification was accompanied by a slight increase in rubber content, lower KOH No., higher L.A.C. stability, and unchanged or slightly lowered viscosity. Mineral content of the latex was reduced, the magnesium content being halved. The clarified latex was found to give a higher d.r.c. when creamed.

Sheet rubber produced from latex after clarification showed a slight reduction in the modulus values of the vulcanisate.

The experimental data suggest that the technical properties of latex or sheet rubber are not likely to benefit sufficiently to justify clarification of field latex. The degree to which lutoids were removed by the process is uncertain, but it is doubtful whether a good separation was obtained. It is hoped to find a means of stabilising the lutoid bodies and effectively removing them by centrifugation, with a view to obtaining products with different and technically valuable properties.

Sulphuric acid as a coagulant — A number of trials have been carried out during the past year in which sulphuric acid has been used as a coagulant in place of formic acid. The work is still proceeding and it would be premature to draw definite conclusions. The evidence so far indicates that little difference in properties, either of raw rubber or of vulcanisates, is likely to result from its use, provided a marked excess of acid is not employed.

Modification of the technical properties of RSS — With the introduction of the classification of rubber according to technical properties, the possibility occurs of manufacturing a rubber to producer's or user's requirements. This could only be achieved where rigid scientific control of factory processes is maintained, but preliminary trials suggest that modification of the modulus level of A.C.S. No. 1 vulcanisates can readily be achieved. The addition of bases such as ammonia or ethylamine to latex before coagulation gives rise to a definite increase in the modulus value. They have the disadvantage that more acid is required for coagulation. Other nitrogenous bases, however, were found to be far more effective than either ammonia or ethylamine. Among the most active substances were quaternary ammonium bases having a long fatty chain, such as cetyl trimethyl ammonium bromide and tetradecyl pyridinium bromide; the addition of 0.02% of these reagents (based upon rubber) to latex prior to coagulation increased the modulus (A.C.S. No. 1 compound) from below 40 to over 60 kg per sq.cm.

Bleaching yellow pigment in latex – The practice of fractional coagulation in order to produce white latex crepe is both time consuming and costly. It has now been observed that the yellow colour can be destroyed by adding to the latex certain reagents prior to coagulation. The effective reagents are mercaptans, which also behave as rubber peptising agents. The amount required for bleaching is considerably less than that normally employed for peptising and little or no softening has been observed in the crepe produced.

A British Patent application has been filed and licences to operate the process granted to a number of estates. Reports from crepe producers using the method have generally been satisfactory, but some estates complained that the product had a grey undertone. Other estates produced a very white product without fractional coagulation and obtained top prices.

IV(3) NEW FACTORY PROCEDURES

Line ahead creping battery – Experiments carried out using a light, line ahead battery for creping coagulum, have demonstrated the feasibility of the scheme, and a prototype machine was in course of construction at the end of the year. Further trials will have to be made before the process can be considered to have been proved. Application has been made for a patent to cover the machine and the process.

Continuous coagulation — During recent years a number of machines have been devised for the purpose of producing dry rubber from latex by a continuous method. A process has been developed in the laboratories of the L.A.C., in which coagulum is produced, washed and dried continuously, in the form of a thin film (0.2 – 0.4 mm thick). The original experiments were, of necessity, carried out with ammonia-preserved latex. A new experimental model for producing the coagulum film from fresh latex has now been set up at the R.R.I. Preliminary trials have disclosed a difficulty in working with fresh latex, namely, the very soft nature of the film immediately after coagulation. Experiments have indicated possible ways of overcoming this difficulty by using appropriate reagents for coagulation. A further complication is the extreme day to day variation in the thickness and other properties of the film produced.

ADVISORY WORK

THE VOLUME OF GENERAL ADVISORY WORK remained much the same as in the previous year. Considerable interest in preparing bleached crepe was shown towards the end of the year and the laboratories assisted in the commercial development of the process by preparing the reagent emulsion required, pending the appearance on the market of a suitable proprietary material.

Office records show the following:

Interviews at the Institute	248
Visits to Estates *etc*	324
Letters & Reports	2,663

Samples examined (excluding samples examined for purposes of Technical Classification) 1,486

Heavy demands have recently been made upon the testing service of the laboratories by H.M. Comptroller of Customs.

The following advisory leaflets and memoranda were issued:

C/AL.13(50)	Rubber Powder.
C/M.52(50)	Second Progress Report Technical Organisation Natural Rubber Producers, Malaya.
C/M.53(50)	Measurement of Modulus at a Fixed Elongation.
C/M.55(50)	Colour of Crepe from Clonal Latex.
C/M.59(50)	Sheeting Batteries Available in Malaya.
C/M.67(50)	Third Progress Report Technical Organisation Natural Rubber Producers, Malaya.
C/M.68(50)	Instructions for Taking Samples from Baled Rubber.
C/M.69(50)	Report on the Singapore Meeting (August 1950) of Technical Representatives of Far Eastern Research Organisations.
C/M.70(50)	Procedure adopted by R.R.I. for sampling, testing and grading rubber according to technical properties.
C/M.78(50)	A note on Creping Batteries.
C/M.79(50)	Preparation of White Latex Crepe.

OTHER ACTIVITIES

TOWARDS THE MIDDLE OF THE YEAR, a contract for the new factory at the R.R.I. Experiment Station was awarded and building commenced. At the end of the year, the factory was nearing completion and the first trial lots of RSS were being produced.

The Head of the Division continued to act as secretary and convenor of a committee of Malayan latex technologists set up to advise the British Standards Institution Sub-Committee on latex testing methods. Comments upon proposed British Standard Specification were forwarded to that Institution.

During the year a Malayan Section of the Institution of the Rubber Industry was inaugurated, the Head of the Division being elected Vice-Chairman of the Section; three members of the Division served on the Committee.

At the end of June, Dr R.G. Newton and the Chemical Engineer, Mr A. Walker, visited Indo-China, to discuss problems of mutual interest with French technologists.

PUBLICATIONS

A REPORT by K.C. ROBERTS, 'The Constituents of Hevea Latex, Part VIII', written before the Japanese Occupation of Malaya was edited and published in the Journal, (*J. Rubb. Res. Inst. Malaya* 12 (1950) 278) as communication 270.

A paper entitled 'Aspects of the problem of obtaining uniform Malayan rubber', by R.G. NEWTON, M.W. PHILPOTT, H. FAIRFIELD-SMITH and W.G. WREN, was presented at the Conference of the American Chemical Society, Rubber Division, held at Cleveland in October. The paper was read by Dr R.G. Newton who also established contacts between the Rubber Research Institute and a number of research organisations in the United States.

W.G. WREN
Head of Chemical Division

Kuala Lumpur
15 May 1951